

A SPECTROSCOPIC STUDY OF THE PRODUCTS OF REDUCTIVE ALKYLATION
OF AN ILLINOIS COAL

Leon M. Stock and Reid S. Willis

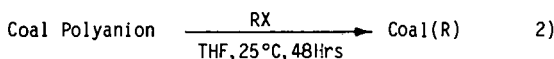
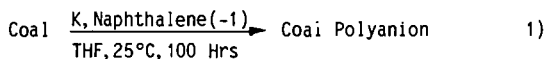
Department of Chemistry, University of Chicago, Chicago, IL 60637

INTRODUCTION

Mild chemical reactions such as alkylation and reductive alkylation provide techniques for the conversion of coal macromolecules into substances that are soluble. The soluble products of such reactions can be investigated by one and two dimensional, high resolution NMR spectroscopy to obtain structural information that is often difficult to obtain by the investigation of solids. Moreover, the soluble products can be subjected to selective chemical transformations to obtain additional information to guide the interpretation of the spectroscopic results. This article concerns the use of a selected series of chemical reactions and nuclear magnetic resonance spectroscopy for the definition of the structural characteristics of the reactive carbanions and oxygen anions formed during the reductive alkylation of an Illinois No. 6 coal.

RESULTS AND DISCUSSION

The reductive alkylation (1,2) of a representative Illinois No. 6 coal, $C_{100}H_{87.0}O_{13.1}S_{1.9}N_{0.75}$, with 8.2 % ash, was carried out as shown.



The reactions were performed and the products were isolated as described previously (3) using methyl, methyl- d_3 , methyl- ^{13}C , and ethyl iodide as the alkylating agents. The yield of tetrahydrofuran-soluble products ranged from 48 to 68% in 15 experiments. Infrared spectroscopy established that the alkylation reaction was complete. In particular, the very typical, broad oxygen-hydrogen stretching frequency was absent in the spectra of the products. The molecular weight distribution of the soluble, alkylated coal was examined by vapor pressure osmometry (4). The results imply that the number average molecular weight of the material obtained after filtration and gel permeation chromatography is about 2000 in pyridine solution.

Several different measurements indicate that about 22 equivalents of potassium are consumed per 100 carbon atoms of this coal during reductive alkylation (3). Analyses of the soluble reaction products obtained in the reaction with methyl- d_3 iodide for deuterium by deuterium nuclear magnetic resonance spectroscopy and by combustion mass spectroscopy (5) indicate that the most soluble products contain 11 ± 1.5 alkyl groups per 100 carbon atoms. The difference between the amount of potassium consumed in the reduction and the degree of alkylation arises, in part, because the reactive

intermediates generated in the reduction reaction abstract hydrogen from tetrahydrofuran. The occurrence of this reaction was demonstrated by conducting the reduction in the presence of labeled tetrahydrofuran and quenching the reaction in water. We estimate that not less than 5 hydrogen atoms are incorporated into the coal macromolecules from the solvent on the basis of the degree of incorporation of deuterium in the experiment and the anticipated primary kinetic isotope effect.

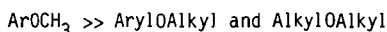
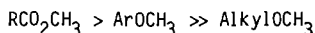
C-Alkylation.--Quantitative analyses of the reaction products obtained using methyl- ^{13}C iodide by carbon NMR spectroscopy indicate that about equal quantities of C- and O-alkylation products are formed (3). Following a leading observation by Ignasiak and his coworkers (6), we also examined the carbon NMR spectrum of the products obtained in a reductive ethylation reaction. There were 5 prominent absorption bands in the spectrum as outlined in Table 1. The resonance at 8.5 ppm is surprisingly intense and implies that the concentration of ethyl groups at saturated, quaternary carbon atoms is quite high. Indeed, quantitative analysis of the spectral data suggest that the carbon alkylation reactions occur preferentially at highly substituted positions and at primary benzylic positions and are compatible with the idea that this coal contains three distinct structures--reactive aryl methyl groups, activated trisubstituted methane fragments, and aromatic structures--that may be alkylated.

O-Alkylation.--The assignments of the resonances of the O-methylation products observed in regions 1, 2, and 3 obtained in the reactions with methyl- ^{13}C iodide, Figure 1, are summarized in Table 2. The assignments presented in column A are based upon chemical shift data exclusively. To obtain more definite information about the structures of the compounds responsible for these resonances, we carried out a series of selective chemical transformations.

First, the soluble reaction products were hydrolyzed using tetrabutylammonium hydroxide in aqueous tetrahydrofuran for 24 hours at room temperature. The solution was acidified with dilute hydrochloric acid and the product was isolated and dried prior to the reexamination of its carbon spectrum. Quantitative measurements of the absorption at 51 ppm revealed that over 98% of the intensity was removed. Hence, the resonances in region 3 arise, virtually exclusively, from alkyl and aryl carboxylic acid esters.

Second, acid hydrolysis was carried out to examine the proposal of Haenel and coworkers (7) that enol methyl ethers may, in part, be responsible for the resonance signals in region 1. The reaction was carried out with 2N hydrochloric acid in aqueous tetrahydrofuran for 48 hours at room temperature. The product was recovered and the NMR spectrum recorded. There was no change in the absolute intensities of the resonance signals in regions 1 and 2. Thus, methyl vinyl ethers are not formed to a measurable degree in the reductive alkylation of the Illinois coal.

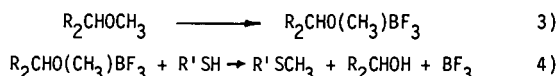
Third, a selective displacement reaction was used to distinguish the methyl alkyl ethers from the methyl aryl ethers. The reaction of the soluble coal with lithium iodide in collidine at 170°C for 24 to 48 hours was used for this purpose. The chemical literature indicates that this reaction is highly selective for the displacement of methyl groups (8).



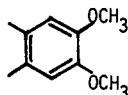
Appropriate control experiments with collidine indicated that the alkylated coal could be recovered unchanged from the reaction medium in the absence of lithium io-

dide. However, when the reaction was carried out with in the presence of the iodide there was a 70% decrease in solubility in tetrahydrofuran. The product was alkylated with unlabeled ethyl iodide to yield a material that was more than 80% soluble in pyridine. The carbon NMR spectrum of this product is greatly altered, Figure 2A. Specifically, the areas of regions 1, 2, and 3 are decreased by 96, 89, and 100%, respectively.

Fourth, it is known (9) that primary and secondary alkyl methyl ethers and benzyl methyl ethers can be cleaved selectively by boron trifluoride-etherate and a thiol, equations 3) and 4).



This reaction was performed with the ^{13}C enriched demethylated coal using 1,2-ethanedithiol at room temperature. The product of the reaction was quite soluble in organic solvents. The changes in the intensities of the resonances at 55 and 58 ppm, Figure 2B, are particularly informative. The signal at 58 ppm has disappeared from the spectrum but the signal at 55 ppm is unaltered. These results imply that the compounds responsible for the residual signal at 58 ppm in Figure 2A are aliphatic methyl ethers and that the compounds responsible for the residual signal at 55 ppm in Figures 2A and 2B are aryl methyl ethers that resist dealkylation by both lithium iodide and borontrifluoride-ethanedithiol. The observations are most consistent with the presence of dimethoxyaryl compounds.



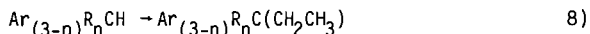
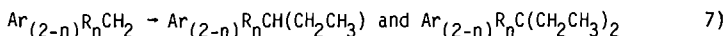
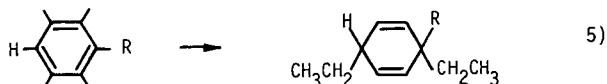
These compounds are known to resist demethylation with lithium iodide and to be inert toward acid-catalyzed cleavage. Thus, we infer that about 4% of the methyl groups added to this coal appear in such structures. The existence of compounds of this type may also be inferred from the differences observed in the nuclear Overhauser effect for the compounds in region 2 relative to the NOE for the other O-alkylation products.

The fact that the acid-catalyzed ether cleavage reaction eliminates the resonance at 58 ppm confirms the assignment of this weak signal to an aliphatic methyl ether. The chemical shift observed for this resonance is in accord with the resonance expected for the carbon atom of the methyl group in a primary alkyl methyl ether, but is incompatible with the signal expected for a simple primary benzyl methyl ether.

CONCLUSION

Reductive alkylation adds about 12.5 alkyl groups/100 carbon atoms to the Illinois No. 6 coal. Broadly speaking 5.5 of these groups are bonded to carbon atoms and 7 are bonded to oxygen atoms. Only very small quantities of nitrogen and sulfur alkylation products can be detected. The spectroscopic results for the reductively

ethylated coal suggest that the C-alkylation reactions proceed via reductive alkylation to yield substituted dihydroaromatic compounds, equation 5), and via base-catalyzed alkylation to yield substituted arylmethanes as shown in equations 6) - 8).



The occurrence of the latter reactions strongly suggests that this Illinois coal contains three or four reasonably strong carbon acids per 100 carbon atoms. The existence of these reaction sites offers new opportunities for other selective transformation reactions.

The results obtained in the spectroscopic investigations of the chemically transformed O-alkylation products provide a reasonable basis for the definition of the relative abundances of the different O-alkylation products. The outcome of the analysis is shown in Column B of Table 2. The new observations provide definite information regarding the occurrence of low, but observable, quantities of alkyl methyl ethers, the presence of significant amounts of highly hindered aryl methyl ethers and dimethoxyaryl compounds and carboxylic acid esters. Our results also exclude several types of compounds. Thus, primary benzylic methyl ethers, secondary and tertiary alkyl methyl ethers as well as vinyl methyl ethers are not present in detectable amounts. We infer that the observed distribution of products in the alkylated coal is comparable to the distribution of these functional groups in the original coal. As a consequence, the new results provide a more secure basis for the discussion of the structure and reactivity of this coal.

REFERENCES

- 1) H.W. Sternberg, C.L. Delle Donne, P. Pantages, E.C. Moroni, and R.E. Markby, Fuel, **50**, 432 (1971).
- 2) The subject has been reviewed, L.M. Stock, Coal Science, **1**, 161 (1982).
- 3) L.B. Alemany and L.M. Stock, Fuel, **61**, 250 (1982).
- 4.) This determination was performed by J.W. Larsen and his students.
- 5) The combustion mass pectral analysis was carried out by Gollob Laboratories.
- 6) N. Cyr, M. Gawlak, D.W. Carson, and B.S. Ignasiak, Fuel, **62**, 412 (1983).
- 7) M.W. Haelnel, R. Mynott, K. Niemann, U.-B. Richter and L. Schanne, Angew. Chem. Int. Ed. Eng. **19**, 636 (1980).
- 8) J.E. McMurry, Org. Reactions, **24**, 187 (1976).

- 9) M. Node, H. Hari, and E. Fujita, J. Chem. Soc. Perkin Trans. I, 2237 (1976).

ACKNOWLEDGEMENT

It is a pleasure to acknowledge the support of this research by the United States Department of Energy and by the Illinois Department of Energy and Natural Resources.

Table 1. The Assignment of Resonances in the Carbon NMR Spectrum of Reductively Ethylated Coal.

Chemical Shift (ppm)	Assignment Resonance of Ethyl Group, Reaction
8.5	Methyl, ethylation at tertiary carbanionic center to form quaternary product, $R_3C(CH_2CH_3)$
12.5	Methyl, ethylation at secondary carbanionic center to form tertiary product, $R_2CH(CH_2CH_3)$
15	Methyl, ethylation at primary carbanionic center to form secondary product, $RCH_2(CH_2CH_3)$ Methyl, ethylation at oxygen, $ArO(CH_2CH_3)$
65	Methylene, ethylation at unhindered aryl oxygen, $ArO(CH_2CH_3)$
69	Methylene, ethylation at hindered aryl oxygen, $R_2ArO(CH_2CH_3)$

Table 2. Column A. The Assignments of the Resonances in the O-Alkylation Region of the Carbon NMR Spectrum of Reductively Methylated Illinois No. 6 Coal. Column B. The Relative Abundances of the O-Alkylation Products Defined by Chemical Conversions and Carbon NMR Spectroscopy.

Column A Possible NMR Assignments	Column B Relative Abundance ^a
1. Region Centered at 61 ppm	Region Centered at 61 ppm
Vinyl ethers	
Primary alkyl ethers	Primary alkyl ethers 0.1
Primary benzyl ethers	
Hindered aryl ethers	Hindered aryl ethers 2.2
2. Region Centered at 55 ppm	Region Centered at 55 ppm
Secondary alkyl ethers	
Unhindered aryl ethers	Unhindered aryl ethers
Dihydroxyaryl compounds	Dihydroxyaryl compounds 0.6
Simple aryl ethers	Simple aryl ethers 3.3
3. Region Centered at 51 ppm	Region Centered at 51 ppm
Tertiary alkyl ethers	
Aryl- and Alkylcarboxylic acid esters	Aryl- and Alkylcarboxylic acid esters 0.8

^aThe results have been normalized on the basis of the analytical results which suggest that there are 7 O-methyl groups per 100 carbon atoms in the alkylated products.

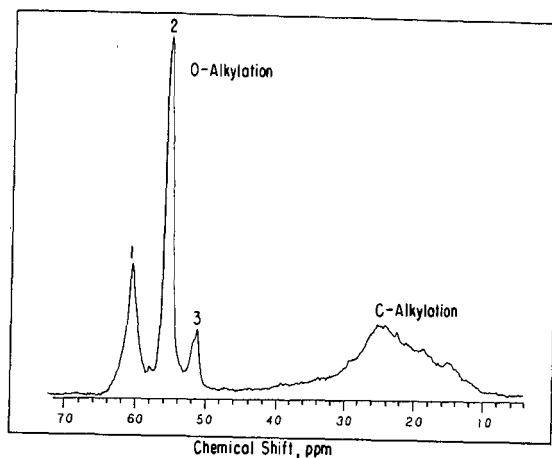


Figure 1.--The carbon nuclear magnetic resonance spectrum of an intermediate molecular weight, gel permeation chromatography fraction of the product of reductive methylation of Illinois No. 6 coal.

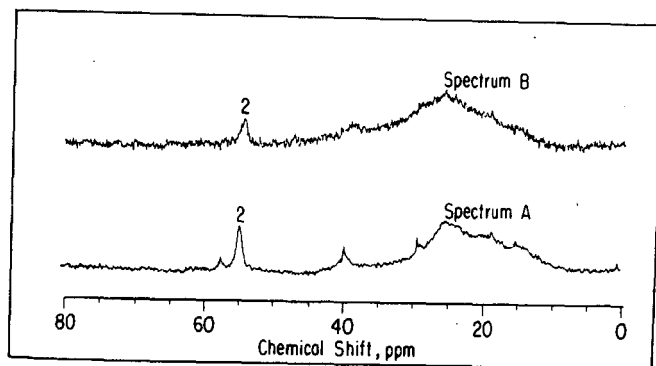


Figure 2.--The carbon nuclear magnetic resonance spectrum of the material shown in Figure 1 (A) after treatment with lithium iodide in collidine and (B) after subsequent treatment with boron trifluoride and ethanedithiol.